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Notes:

1. Untranslatable words are replaced with asterisks (***).
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CLAIM + DETAILED DESCRIPTION

[Claim(s)]

[Claim 1] In a method of manufacturing a polymer by carrying out suspension polymerization of the monomeric mixture containing vinyl chloride or vinyl chloride in curing units provided with a reflux condenser, By the time a cooling start postpolymerisation invert ratio by said reflux condenser reaches to 60%, 10 hour half life period temperature in 0.1 mol/L concentration in benzene has the process of teaching a hyperactive oil soluble polymerization initiator 40 ** or less, A charge of said oil soluble polymerization initiator is 0.0001 to 0.02 weight section per monomer 100 weight section, and preparation velocity of said oil soluble polymerization initiator is the aforementioned charge per for 1 minute. A manufacturing method of a polymer being 0.5 to 5 weight %.

[Detailed Description of the Invention]**[0001]**

[Industrial Application] This invention relates to the manufacturing method of the polymer by suspension polymerization of the monomeric mixture containing vinyl chloride or vinyl chloride.

[0002]

[Description of the Prior Art] Generally, [suspension polymerization of the monomeric mixture (henceforth vinyl chloride etc.) containing vinyl chloride or vinyl chloride] A jacket and a reflux condenser in the curing units which it had For example, an aqueous medium, Teach a dispersant (suspension) and a polymerization initiator, and next exhaust the inside of curing units and vinyl chloride etc. are taught, A rise in temperature is carried out after preparing other various additives if needed until it reaches a predetermined polymerization reaction temperature in a jacket in the inside of curing units through hot water, Then, it carries out by

the method of making a polymerization reaction perform, holding the inside of curing units to predetermined reaction temperature by removing polymerization reaction heat through cooling water to a jacket and a reflux condenser.

[0003]In recent years, in order to improve productivity, shortening of polymerization time is attained. There is a method of increasing the quantity of the charge of a polymerization initiator as one of the methods of shortening of polymerization time, and increasing polymerization reaction velocity. When based on this method, it is necessary to heighten the cooling capability in the stage which starts since the calorific power by a polymerization reaction increases from the early stage of a polymerization. (However, the early stage of a polymerization, i.e., time when a polymerization reaction start postpolymerisation invert ratio is low, (usually less than 15% of polymerization conversion) If cooling by a reflux condenser is performed) Since the polymer obtained has inconvenience of it being generated by the coarse grain or a block-like polymer generating, a reflux condenser cannot be used at this time. Therefore, only the jacket had to perform cooling in the early stage of a polymerization, and the problem that cooling capability was insufficient was produced.

[0004]

[Problem to be solved by the invention]. In order to avoid the above problems, use ** subvitality polymerization initiator together. ** Divide and teach a polymerization initiator to 2 times after reaching predetermined polymerization conversion polymerization reaction start before, It controls to stop the polymerization reaction velocity in the early stage of a polymerization, to make calorific power small, and not to exceed the cooling capability of a jacket, and the measure of increasing polymerization reaction velocity after the cooling start by a reflux condenser is taken.

[0005]By the way, in order to shorten polymerization time, it is necessary to cool efficiently. However, since polymerization reaction velocity is increased after the cooling start by a reflux condenser according to the method of above-mentioned ** and **, the peak of generation of heat will be greeted in the second half of a polymerization reaction. Therefore, the unused portion of the cooling capability by a reflux condenser cannot say that and the efficiency of cooling is good immediately after the start of cooling by a reflux condenser.

[0006]It is called an initial color, and the coloring peculiar to a polymer produced when processing a polymer into the moldings of a sheet etc., without adding a colorant etc. is so preferred that it is small.

[0007]However, since the polymerization time after a subvitality polymerization initiator remains in a polymer and reaches predetermined polymerization conversion in the method of above-mentioned ** in the method of above-mentioned ** is short, the polymerization initiator taught to the 2nd time remains in a polymer. Therefore, according to the method of above-mentioned ** and **, there is inconvenience that the initial color nature at the time of fabricating

the polymer obtained on a sheet etc. gets worse.

[0008]Therefore, SUBJECT of this invention is the method of manufacturing a polymer by carrying out suspension polymerization of the vinyl chloride etc. in curing units provided with the reflux condenser, When it can cool efficiently, polymerization time can be shortened and it moreover fabricates on a sheet etc., there is the initial color nature of the moldings acquired in providing the manufacturing method which can manufacture a good polymer.

[0009]

[Means for solving problem]This invention persons solved above-mentioned SUBJECT, as a result of repeating research wholeheartedly. In the method of manufacturing a polymer when this invention carries out suspension polymerization of the monomeric mixture containing vinyl chloride or vinyl chloride in curing units provided with the reflux condenser, By the time the cooling start postpolymerisation invert ratio by said reflux condenser reaches to 60%, 10 hour half life period temperature in the 0.1 mol/L concentration in benzene has the process of teaching a hyperactive oil soluble polymerization initiator 40 ** or less, The charge of said oil soluble polymerization initiator is 0.0001 to 0.02 weight section per monomer 100 weight section, and the preparation velocity of said oil soluble polymerization initiator is the aforementioned charge per for 1 minute. The manufacturing method of the polymer being 0.5 to 5 weight % is provided.

[0010]In hyperactive oil soluble polymerization initiator this invention, 10 hour half life period temperature in the 0.1 mol/L concentration in benzene used, [as a hyperactive oil soluble polymerization initiator 40 ** or less] Acetyl-cyclohexyl-sulfonyl-peroxide (10 hour half life period temperature in the 0.1 mol/L concentration in benzene: 26.5 **), Isobutyryl peroxide (said 32.5 **) and alpha-cumilperoxy neodecanoate (said 36.6 **), diisopropylbenzene (said 36.4 **) and diaryl peroxy carbonate (said 38.3 **) etc. -- it is mentioned, and even when these are independent, even if they combine two or more sorts, they can be used. Things desirable in these hyperactive oil soluble polymerization initiators are isobutyryl peroxide and alpha-cumilperoxy neodecanoate.

[0011]60%, by the time the cooling start postpolymerisation invert ratio according [the specified quantity of the above-mentioned hyperactive oil soluble polymerization initiator] to a reflux condenser reaches to 50% preferably, it will be taught at predetermined preparation velocity. Thereby, polymerization time can be shortened and the polymer in which moldings with good initial color nature are moreover acquired can be manufactured. If addition of said hyperactive oil soluble polymerization initiator is started before the cooling start by a reflux condenser, The inconvenience that it becomes difficult for the limit of the cooling capability of a jacket to be exceeded according to increase of polymerization reaction heat, and to maintain the temperature in curing units to a predetermined temperature, or the fisheye in the polymer obtained increases arises. On the other hand, after polymerization conversion exceeds 60%,

when said hyperactive oil soluble polymerization initiator is added, the residual volume of this initiator in a polymer will increase, and the initial color nature at the time of fabricating this polymer will get worse.

[0012]The charge of the above-mentioned hyperactive oil soluble polymerization initiator is 0.0001 to 0.02 weight section per monomer 100 weight section, and is 0.001 to 0.01 weight section preferably. The initial color nature at the time of the residual volume of this initiator in the polymer obtained increasing, and fabricating this polymer, when there were too many charges of the above-mentioned hyperactive oil soluble polymerization initiator is reduced, and if too small, polymerization time can seldom be shortened.

[0013]Preparation velocity of the above-mentioned hyperactive oil soluble polymerization initiator is the aforementioned charge per for 1 minute. It is 0.5 to 5 weight %, and is 1 to 3 weight % preferably. If preparation velocity of the above-mentioned hyperactive oil soluble polymerization initiator is too large, calorific power by a polymerization reaction will increase rapidly, and inconvenience, like it becomes difficult for cooling capability by jacket and a reflux condenser to be insufficient, and to control temperature in curing units uniformly arises. If said preparation velocity is too small, an unused portion of cooling capability of this capacitor immediately after a start of cooling by a reflux condenser will increase, and inconvenience of cooling efficiency seldom being able to shorten polymerization time bad will arise.

[0014]Manufacture of a polymer by suspension polymerization, such as vinyl chloride in polymer manufacturing method this invention, is carried out as follows, for example. First, other additives are prepared [a polymerization initiator and if needed] other than the above-mentioned hyperactive oil soluble polymerization initiator which prepare an aqueous medium and a dispersant, next teach vinyl chloride after exhaust air, etc. to curing units provided with a jacket and a reflux condenser, and are still more generally used for them in inside of these curing units. Then, a polymerization reaction is made to start by carrying out the rise in temperature of the inside of these curing units to predetermined polymerization temperature. It is made to react after a polymerization reaction start, starting removal of through and polymerization reaction heat for cooling water in a jacket, and holding temperature in curing units uniformly. Next, if polymerization conversion of a preparation monomer reaches to not less than 15%, cooling by a reflux condenser will be started. A grain size of a polymer which will be obtained if start time of cooling by a reflux condenser is too early may become coarse, or a block-like polymer may generate, and polymerization time cannot be shortened if too late. By the time a postpolymerisation invert ratio which started cooling by a reflux condenser reached to 60%, as it described above, the specified quantity of said hyperactive oil soluble polymerization initiator is taught at predetermined preparation velocity. After an end of a polymerization collects unreacted monomers, and extracts a generated polymer out of curing units.

[0015][the monomer which polymerizes with the application of the manufacturing method of this invention] [as a comonomer which the monomeric mixture (usually 50 weight % or more of vinyl chloride) which uses vinyl chloride besides a vinyl chloride independent as a subject is included, and copolymerizes with this vinyl chloride] For example, acrylic ester and methacrylic acid ester, such as vinyl ester; methyl acrylate, such as vinyl acetate and vinyl propionate, and ethyl acrylate; for example, Olefin; maleic anhydride; acrylonitrile; styrene; vinylidene chloride, such as ethylene and propylene; in addition to this, vinyl chloride and a copolymerizable monomer are illustrated.

[0016]As polymerization initiators other than the above-mentioned hyperactive oil soluble polymerization initiator first taught to curing units in the above-mentioned manufacturing method, 10 hour half life period temperature in the 0.1 mol/L concentration in benzene uses the subvitality polymerization initiator which is 55 ** or less exceeding 40 **. As this subvitality polymerization initiator, for example Diisopropyl peroxy dicarbonate (10 hour half life period temperature in the 0.1 mol/L concentration in benzene: 40.5 **), di-ethylhexylperoxydicarbonate (said 43.4 **) etc. -- a peroxy carbonate compound. t-hexyl peroxy pivalate (said 53.2 **) and t-butylperoxy neodecanoate (said 46.5 **), t-hexylperoxy neodecanoate (said 49.7 **) etc. -- peroxy ester compound, 2, and 2-azobis 2,4-dimethylvaleronitrile (said 51.0 **) etc. -- an azo compound etc. are mentioned, and even when these are independent, even if they combine two or more sorts, they can be used. In the range which does not exceed the cooling capability the jacket independent before the cooling start by a reflux condenser, what is necessary is just to set up the charge of this subvitality polymerization initiator suitably, and preferably, It is 0.03 to 0.12 weight section per preparation monomer 100 weight section, and is 0.05 to 0.08 weight section still more preferably. It becomes a cause by which the initial color nature at the time of fabricating the polymer obtained on a sheet etc. when there were too many charges of this polymerization initiator gets worse, and if too small, shortening of polymerization time cannot be attained but it will become a cause of a productivity slowdown.

[0017]per preparation monomer 100 weight section, the quantity of the aqueous medium prepared in the above-mentioned manufacturing method is 100-200 weight section, and is usually preferred -- it is 110-160 weight section.

[0018][the dispersant prepared in the above-mentioned manufacturing method] Conventionally, it may be publicly known and For example, methyl cellulose, hydroxyethyl cellulose, Water-soluble-cellulose-ether; partial saponification polyvinyl alcohol; acrylic acid polymers, such as hydroxypropylcellulose and hydroxypropylmethylcellulose; water-soluble polymer, such as gelatin, is mentioned. Even if these are independent, they can use even two or more sorts of combination. With the aforementioned dispersant, sorbitan monolaurate, a sorbitan trio rate, Nonionic emulsifiers, such as glycerol tristearate and ethylene oxide

propylene oxide block copolymer, Anionic emulsifiers, such as polyoxyethylene sorbitan monolaurate, polyoxyethylene glycerol olate, and lauryl acid sodium, etc. can also be used. The charges of a dispersant are usually 0.03-2.0 per preparation monomer 100 weight section. It is a weight section and is 0.04 to 0.15 weight section preferably.

[0019]It is also arbitrary to add a modifier, a chain transfer agent, pH adjustor, a gelling improving agent, an antistatic agent, scale inhibitor, etc. which are suitably used for the polymerization of a vinyl chloride system as other additives if needed.

[0020]What is necessary is just to perform the preparation methods, such as other comonomers and a dispersant, by a publicly known method conventionally depending on other conditions for this polymerization, for example, the aqueous medium to curing units, a vinyl chloride monomer, and the case, and they may be conventionally publicly known. [of polymerization conditions, such as polymerization temperature,]

[0021]

[Working example]Hereafter, an example is given and the polymer manufacturing method in this invention is explained.

As embodiment 1 curing units, the curing units made from stainless steel of content volume [of 2 m] ³ provided with the jacket (the maximum cooling capability: 70 Mcal/Hr) and the reflux condenser (the maximum cooling capability: 50 Mcal/Hr) were used. In consideration of the safety of an experiment, it experimented by setting the cooling capability of a jacket as 55 Mcal/Hr, and setting the cooling capability of a reflux condenser as 45 Mcal/Hr. To said curing units, it is deionized water. 856 kg, partial saponification polyvinyl alcohol 206g and the cellulose ether 137g are thrown in, Teaching 685 kg of vinyl chloride monomers, then agitating the reaction mixture in curing units, after deaerating the inside of these curing units until it is set to 50mmHg. It is di-2- ethylhexylperoxydicarbonate as a subvitality polymerization initiator as a polymerization initiator (1). (10 hour half life period temperature in the 0.1 mol/L concentration in benzene: 43.4 **) 190 g, T-butylperoxy neodecanoate (the half-life temperature: 46.5 **) 190 g was pressed fit with the pump. Then, the rise in temperature of the inside of curing units was carried out to said jacket to 57 ** through hot water, next the temperature in curing units was polymerized by holding at 57 ** through cooling water in this jacket.

[0022]It is isobutyryl peroxide as a polymerization initiator (2) in said curing units at the same time it starts cooling by said reflux condenser, when polymerization conversion reaches to 15%. (the half-life temperature: 32.5 **) Addition was started. The charge of isobutyryl peroxide is 60g and preparation velocity was 1 g per for 1 minute. The polymerization conversion at the time of addition of isobutyryl peroxide being completed was 40%.

[0023]When it polymerized succeedingly and the internal pressure of said curing units fell to 6.0kgf/cm² and G, after suspending the polymerization reaction and collecting unreacted

monomers, slurry which is a reaction mixture was taken out from curing units, dehydration desiccation was carried out, and the vinyl chloride polymer was obtained. The time (polymerization time) required by the stop of a polymerization reaction from the rise-in-temperature start is shown in Table 1.

[0024]In order to evaluate the initial color nature at the time of fabricating the obtained vinyl chloride polymer on a sheet, the chroma TEKKUNESU index (b value) was measured by the following method. The result is shown in Table 1.

[0025]- measurement profit **** vinyl chloride polymer 100 weight section of a b value, and a lauric acid tin series stabilizer (Showa -- insulation study company make.) As TS-101 1 weight section, cadmium stabilizer (Katsuta chemically-modified company make, C-100 J) 0.5 weight section, and a plasticizer, dioctyl phthalate 50 weight section is blended and 2 roll mills are used. Thickness after kneading for 5 minutes at 150 ** A 0.8-mm sheet was formed. Next, this sheet was cut out and it put into the mold of 4cmx4cmx 1.5cm (thickness) in piles, and by 150 ** and 65 - 70kgf/cm², it heated, and pressing was carried out and the test portion was created. Using the photoelectric colorimeter (made by Nippon Denshoku Industries Co., Ltd.), JIS Z 8730 (1980) was asked for the chroma TEKKUNESU index b value in the color difference formula of the hunter of a description, and the degree of **** estimated this test portion small that initial color nature is good, so that the b value was small.

[0026]A b value is calculated as follows. According to the description of JIS Z 8722, the stimulus values Y and Z of an XYZ colorimetric system are calculated with photoelectric tristimulus colorimetry using the standard light C and a photoelectric colorimeter (the Nippon Denshoku Industries Co., Ltd. make, Z-1001 DP type colorimetric color difference meter). The conditions d of the description were adopted as 8722 JIS Z4.3.1 paragraph as a geometric condition of Lighting Sub-Division and light-receiving. From the calculated stimulus values Y and Z, a b value is computed by formula: $b = 7.0 (Y - 0.87Z) / Y^{1/2}$ of a description JISZ 8730 (1980).

[0027]The number of the fisheye at the time of fabricating the obtained polymer on a sheet was measured by the following method. The result is shown in Table 1.

[0028]- Measurement profitable **** vinyl chloride polymer 100 weight section of a fisheye, Dioctyl phthalate 50 weight section, tribasic acid lead sulfate 0.5 weight section, lead stearate 1.5 weight section, [25 g of the mixture prepared by the blending ratio of titanium oxide 0.1 weight section and carbon black 0.05 weight section] 6-inch roll for kneading 10 mm in width, thickness after kneading for 5 minutes at 140 ** The number of the transparent particle number per sheet 100cm² (fisheye) obtained by fabricating on a 0.2-mm sheet was calculated.

[0029]In the one comparative example comparative example 1, it polymerized like Embodiment 1 except not having added isobutyryl peroxide after the cooling start by a reflux condenser. Polymerization time is shown in Table 1. In order to evaluate the initial color nature

at the time of fabricating the obtained vinyl chloride polymer on a sheet, the b value was measured by the same method as Embodiment 1. The result is shown in Table 1. The number of the fisheye at the time of fabricating the obtained vinyl chloride polymer on a sheet was measured by the same method as Embodiment 1. The result is shown in Table 1.

[0030]In the two comparative example comparative example 2, it polymerized like Embodiment 1 except the preparation velocity of isobutyryl peroxide having been 10 g per for 1 minute. Polymerization time is shown in Table 1. The polymerization conversion at the time of the end of addition of isobutyryl peroxide was 25%.

[0031]Since the preparation velocity of isobutyryl peroxide was large in this comparative example 2, Polymerization reaction velocity increased rapidly, calorific power increased rapidly, it becomes impossible for cooling by the jacket and a reflux condenser to have met the deadline temporarily near 30% of polymerization conversion, and temperature in curing units could not be controlled at 57 **, but the temperature in curing units has risen by about 3 **.

[0032]In order to evaluate the initial color nature at the time of fabricating the obtained vinyl chloride polymer on a sheet, the b value was measured by the same method as Embodiment 1. The result is shown in Table 1. The number of the fisheye at the time of fabricating the obtained vinyl chloride polymer on a sheet was measured by the same method as Embodiment 1. The result is shown in Table 1.

[0033]In the three comparative example comparative example 3, it is di-2-ethylhexylperoxydicarbonate as a polymerization initiator (1). 190g and t-butylperoxy neodecanoate It adds to 190 g, 3,5,5-trimethylhexanoyl peroxide (10 hour half life period temperature in concentration 0.1 mol/L in benzene: 59.5 **) 80 g is used, And it polymerized like Embodiment 1 except not having added isobutyryl peroxide after the cooling start by a reflux condenser. Polymerization time is shown in Table 1. In order to evaluate the initial color nature at the time of fabricating the obtained vinyl chloride polymer on a sheet, the b value was measured by the same method as Embodiment 1. The result is shown in Table 1. The number of the fisheye at the time of fabricating the obtained vinyl chloride polymer on a sheet was measured by the same method as Embodiment 1. The result is shown in Table 1.

[0034]In the four comparative example comparative example 4, it is di-2-ethylhexylperoxydicarbonate as a polymerization initiator (1). 190g and t-butylperoxy neodecanoate [instead of 190 g] Di-2- Ethylhexylperoxydicarbonate 184g and t-butylperoxy neodecanoate 184 g is used, And 46g of di-2- ethylhexylperoxydicarbonate and 46 g of t-butylperoxy neodecanoate are used instead of isobutyryl peroxide as a polymerization initiator (2) after the cooling start by a reflux condenser, It polymerized like Embodiment 1 except having added each simultaneously at preparation velocity of 1 g per for 1 minute (it is got blocked and adds at preparation velocity of 2 g per for 1 minute as a polymerization initiator (2)). Polymerization time is shown in Table 1. The polymerization conversion at the end time of

addition of 46g of di-2- ethylhexylperoxydicarbonate and 46 g of t-butylperoxy neodecanoate was 45%. In order to evaluate the initial color nature at the time of fabricating the obtained vinyl chloride polymer on a sheet, the b value was measured by the same method as Embodiment 1. The result is shown in Table 1. The number of the fisheye at the time of fabricating the obtained vinyl chloride polymer on a sheet was measured by the same method as Embodiment 1. The result is shown in Table 1.

[0035]In the five comparative example comparative example 5, it is di-2-ethylhexylperoxydicarbonate as a polymerization initiator (1). 190g and t-butylperoxy neodecanoate It adds to 190 g, 40 g of isobutyryl peroxide was used and, moreover, it polymerized like Embodiment 1 except not having added isobutyryl peroxide after the cooling start by a reflux condenser. Polymerization time is shown in Table 1. In order to evaluate the initial color nature at the time of fabricating the obtained vinyl chloride polymer on a sheet, the b value was measured by the same method as Embodiment 1. The result is shown in Table 1. The number of the fisheye at the time of fabricating the obtained vinyl chloride polymer on a sheet was measured by the same method as Embodiment 1. The result is shown in Table 1.

[0036]

[Table 1]

重合開始剤(1) (g)		実施例 1	比較例 1	比較例 2	比較例 3	比較例 4	比較例 5
()内：単量体 100重量部当 りの仕込み量 (重量部)	重合開始剤 A	190 (0.0277)	190 (0.0277)	190 (0.0277)	190 (0.0277)	184 (0.0269)	190 (0.0277)
	重合開始剤 B	190 (0.0277)	190 (0.0277)	190 (0.0277)	190 (0.0277)	184 (0.0269)	190 (0.0277)
	重合開始剤 C	—	—	—	80 (0.0117)	—	—
	重合開始剤 D	—	—	—	—	—	40 (0.0058)
()内：単量体 100重量部当 りの仕込み量 (重量部)	重合開始剤 A	—	—	—	—	46 (0.0067)	—
	重合開始剤 B	—	—	—	—	46 (0.0067)	—
	重合開始剤 D	60 (0.0088)	—	60 (0.0088)	—	—	—
重合開始剤(2) の仕込み速度		1 g / 分	—	10 g / 分	—	2 g / 分 (それぞれg/分)	—
重合時間		4 時間17分	5 時間 3 分	4 時間20分	4 時間32分	4 時間27分	4 時間30分
b 値		9.4	10.1	9.7	12.5	12.5	9.7
フィッシュアイ (個)		12	11	15	13	13	34

重合開始剤A：ジ-2-エチルヘキシルパーオキシジカーボネート (半減期温度：43.4℃)
 重合開始剤B：t-ブチルパーオキシネオデカノエート (半減期温度：46.5℃)
 重合開始剤C：3,5,5-トリメチルヘキサンイルパーオキシド (半減期温度：59.5℃)
 重合開始剤D：イソブチルパーオキシド (半減期温度：32.5℃)

[0037]

[Effect of the Invention]According to the manufacturing method of this invention, during polymer manufacture, it can cool efficiently, and since the time which polymerization 1 batch

takes can be shortened, productivity improves. When the polymer obtained with the application of the manufacturing method of this invention is fabricated on a sheet etc., there are few fisheyes and initial color nature can acquire good moldings.

[Translation done.]